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For two-letter codes and other abbreviations, refer to the "Guid-
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(54) Title: METHOD FOR IMPROVING SOFTNESS AND WRINKLE REDUCTION OF FABRICS

(57) Abstract: The present disclosure relates to durable wrinkle reduction products that have improved softness. In a preferred embodiment, silicone containing compounds are incorporated into the cross-linked matrix of cellulosic fibres.

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METHOD FOR IMPROVING SOFTNESS AND WRINKLE REDUCTION OF FABRICS

FIELD

5

The present disclosure relates to laundry product compositions that provide substrates, such as fabrics, with durable wrinkle reduction benefits and with improved softness. The composition can be used in both domestic and industrial processes.

BACKGROUND

Durable press treatments (a.k.a. "permanent" press treatments) in the textile industry are well known. In the 1960's, it was known to use polycarboxylic acids for permanent press treatment of textiles. Generally, cellulose fibre can be cross-linked and esterified with polycarboxylic acids, particularly those with two or more carboxylic acid groups. Esterification is achieved upon heating the treated cellulose fibres such as by ironing or other from of heat pressing. Curing catalysts, such as phosphorous containing salts, are also known and serve to aid cross-linking. The

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treated and cured textile is generally strengthened and is less likely to wrinkle during use. Examples of US patents relating to durable press finishing of cotton textile with polycarboxylic acids include: 4,820,307 (Welch et al.),
5 4,975,209 (Welch et al.) and 5,221,285 (Andrews et al.).
The contents of these patents are incorporated by reference.

A disadvantage of known durable press treatments is that the treated and cured textile is typically less soft as
10 compared to the uncured textile. In order to increase softness, inert nonionic or anionic materials have been proposed in formulations as fabric softeners. These softeners include polyethylene, polypropylene and silicone softeners. A disadvantage of these softeners is that they
15 require an additional treatment step subsequent to the durable press treatment and are not durable.

Therefore, there is a need for durable press treatments that not only impart wrinkle reduction benefits but also
20 impart softness benefits, i.e. durable softness. It would be preferable if the softness benefits could be achieved without additional steps subsequent to the durable press treatment.

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SUMMARY

The present disclosure relates to durable wrinkle reduction products that impart durable softness. The products can be any substrate that have hydroxyl groups capable of forming cross-linked matrices. If the substrate is a fabric, the softness benefits are realised, for example, after machine or line drying.

10 In a preferred embodiment, silicone containing compounds are incorporated into the cross-linked matrix of cellulosic fibres of fabric. This is achieved by either 1) reacting the hydroxyl groups of the cellulosic fibres with polycarboxylic acids, wherein the polycarboxylic acids have
15 silicone containing molecules and/or 2) by reacting other molecules having both hydroxyl groups and one or more silicones with the cross-linked polycarboxylic acid/cellulose matrix. It is believed that the incorporated silicone molecules will provide lubrication of the fibre
20 surfaces, resulting in wrinkle reduction, softening and less abrasion on the fibre surface. A most preferred embodiment includes silicone carboxylates, however any silicone compound containing a hydroxy or silanol group or other

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functional group that can react with the cross-linked matrix can provide the desired affect. When cured to form an ester, the silicone containing molecules are difficult to remove under normal wash and wear conditions.

5

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Durable press treatment of cellulosic fibres is
10 achieved by the esterification of cellulosic hydroxyl groups with polycarboxylic acids. The present disclosure of durable softness is achieved by including silicone carboxylates into the formulations. Silanols and hydroxy
15 incorporated into the cross-linked matrix by reacting with (i.e. another esterification reaction) with the polycarboxylic acid.

Other molecules containing multiple hydroxyl groups,
20 such as triethanol amine, can be incorporated into the cross-linked matrix. The silicone carboxylates could also react with these molecules.

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The durable softness compounds are preferably selected from the following molecular classes: silicon carboxylates; silanol fluids; Silanols and hydroxy containing organically modified silicone fluids. Most preferred compounds are

5 carboxylic acid derivatized silicones that include any silicone with a -COOH group. These compounds are preferably incorporated into formulations useful for forming cross-linked matrices with cellulosic fibres. Preferred compounds for forming cross-linked matrices include, for

10 example, 1,2,3,4 cyclopentanetetracarboxylic acid, 1,2,3,4 butanetetracarboxylic acid (BTCA) and polyacrylic acids. Other suitable carboxylic acids are disclosed in the above-cited patents and in U.S. Patent 5,965,517 (Mooney), the contents of which are incorporated herein by reference.

15

A highly preferred composition in accordance with the present disclosure is Monosil® PCA (polysiloxyl pyrrolidone carboxylic acid, CAS number 179005-03-9) available from Mona Industries, Easley, SC., which is included with BTCA to form

20 the desired cross-linked matrix.

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EXAMPLES

The following formulations were made by: 1) adding the ingredients in the order indicated to about 50g water for 5 each 100g of formulation; 2) stirring until homogeneous; and 3) adding water to the final weight while stirring. SDS is sodium dodecyl benzene sulfonate.

Example A

10	Ingredient	Activity	grams/100g	(wt. %)
	BTCA	35.0%	18.0	
	NaHPO ₂	100.0%	1.0	
	Malic Acid	100.0%	1.8	
	PCA (Monosil)	100.0%	0.0	
15	SDS	100.0%	0.0	
	Water	100.0%	79.2	

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Example B

	Ingredient	Activity	grams/100g (wt.)
5	BTCA	35.0%	18.0
	NaHPO ₂	100.0%	1.0
	Malic Acid	100.0%	1.8
	PCA (Monosil)	100.0%	0.0
	SDS	100.0%	3.0
10	Water	100.0%	76.2

Example C

	Ingredient	Activity	grams/100g (wt%)
	BTCA	35.0%	18.0
15	NaHPO ₂	100.0%	1.0
	Malic Acid	100.0%	1.8
	PCA (Monosil)	100.0%	2.0
	SDS	100.0%	3.0
	Water	100.0%	74.2

20

The above formulations were tested for both wrinkle reduction and softness qualities. Formulation A is the control, formulation B has 3% SDS and formulation C features

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3wt% SDS and 2wt% Monosil® PCA. Cotton cloths were processed as follows: 1) soaked in the respective formulations for five (5) minutes; 2) dried overnight; 3) ironed (cotton setting); 4) laundered in a Kenmore® series 5 90 machine set to hot wash/cold rinse (12 minute regular cycle) using all® laundry; and 5) dried in a Kenmore® series 90 electric dryer on cotton (high) setting (50 minute cycle). Wrinkle and softness data were taken after a first wash. Additional wrinkle and softness data were taken after 10 four more washes to investigate softness durability.

Wrinkle reduction was measured by using the American Association of Textile Chemists and Colorists' (AATCC) method # 124, Appearance of Fabrics after Repeated Home 15 Laundering. In this method, cloths are washed and dried. The dried cloths are then evaluated for wrinkle content by comparison with wrinkle smoothness replicas that can be purchased from AATCC. Factors such as the light used, the angle of the cloths and replicas to the light, and the 20 background are carefully controlled and described in the method. There are six replicas with values of 1, 2, 3, 3.5, 4, and 5 with 5 being perfectly smooth and 1 being very wrinkled. Three trained observers are asked to give a value

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of 1-5, to the nearest 0.5 unit, to each cloth based on which replica it most closely resembles. The results are totalled and averaged over the three observers. According to the method, a difference of greater than 0.17 between the results for two products indicates there is a significant difference at the 95% confidence level. A difference of greater than or equal to 0.25 indicates a significant difference at the 99% confidence level

10 **FIRST WASH - wrinkle results**

Formulation	Observer 1	Observer 2	Observer 3	Average
A	2.67	2.67	3.0	2.78
B	2.17	2.83	2.83	2.61
C	2.67	3.17	3.17	3.0

15

As shown in the above data Formulation C had perceptible wrinkle reduction qualities with a confidence level exceeding 99 percent.

20 The cloths after the first wash were also observed for softness, wherein the observers chose those that which felt soft. Observer A chose three cloths, all washed with formulation C. Observer B chose three cloths washed with

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formulation C and one cloth washed with formulation B.

Observer C chose two cloths from formulation C (observer C was unable to choose a third cloth based on softness).

- 5 The cloths from the above tests were washed four more times, as described above. The following wrinkle and softness data were obtained.

After Five washes WASH - wrinkle results

10	Formulation	Observer 1	Observer 2	Observer 3	Average
	A	2.5	2.67	2.67	2.61
	B	2.0	2.5	2.67	2.31
	C	3.0	2.83	3.0	2.94

- 15 The above data shows consistent wrinkle reducing properties in at least the 99% confidence level.

20 The cloths after the five washes were also observed for softness, wherein the observers were asked to choose three cloths that felt softest. Observer A chose three cloths, all washed with formulation C. Observer B chose two cloths washed with formulation C (a third was not chosen). Observer C chose three cloths from formulation C.

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As such, the incorporation of silicone in the cross-linked matrix of the cellulosic fibres exhibits not only durable press properties, but durable softness properties.

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CLAIMS

1. A method for treating a fabric comprising, in no particular order, the steps of:

- 5 (a) contacting a hydroxy comprising fabric with at least one combination selected from the group consisting of a first compound and a second compound, the first compound and a third compound, and the second compound and the third compound; and
- 10 (b) allowing the first and second compound to react with a hydroxy group of the fabric, or allowing the first or second compound to react with a hydroxy group of the fabric and the third compound to react with the first or second compound, or both.

15

2. A method for treating a fabric according to claim 1 further comprising the step of pressing the hydroxy comprising fabric after steps a and b.

- 20 3. A method for treating a fabric according to claim 1 or claim 2 wherein the first composition is a polycarboxylic acid, the second composition is a functionalised siloxane and the third composition is a silanol.

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4. A method for treating a fabric according to claim 3
wherein the polycarboxylic acid is butane tetra carboxylic
acid, the functionalised siloxane is a carboxylic acid
5 functionalised siloxane and the silanol is a polyhydroxy
silanol.

5. A method for treating a fabric according to any
preceding claim wherein the method further comprises the
10 step of contacting the hydroxy comprising fabric with a
fourth compound, the fourth compound comprising at least one
hydroxy group.

6. A method for treating a fabric according to claim 5
15 wherein the fourth compound is triethanol amine.

7. A method for treating a fabric according to any
preceding claim wherein the fabric comprises cellulose-
comprising fibres.

20

8. A method for treating a fabric according to any
preceding claim wherein the first compound is a cyclopentane
tetracarboxylic acid or a polyacrylic acid.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/12536

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D3/20 C11D3/16 C11D3/37 D06M13/192 D06M13/50
D06M13/507 D06M15/643

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 975 209 A (WELCH CLARK M ET AL) 4 December 1990 (1990-12-04) cited in the application column 3, line 8-58 column 6, line 42 -column 8, line 12; claims 1,4,14-16; examples	3-8
Y	US 5 173 201 A (BUZZEE SHEILA G ET AL) 22 December 1992 (1992-12-22) the whole document	3-8
Y	EP 0 523 910 A (DOW CORNING) 20 January 1993 (1993-01-20) page 2, line 9-21 page 3, line 15-28	3-8
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

4 May 2001

Date of mailing of the international search report

16.05.01

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/EP 00/12536

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 235 082 A (HILL RANDAL M ET AL) 10 August 1993 (1993-08-10) column 1, line 6 -column 2, line 4 _____	3-8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 00/12536

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: claims 1 and 2 and claims 5 to 8 when combined with claim 1 or 2

Present claims 1 and 2 and claims 5 to 8 when combined with claim 1 or 2 relate to an extremely large number of possible methods. In fact, the claims contain so many options, due to the absence of definition of the compounds, that a lack of conciseness within the meaning of Article 6 PCT arises to such an extent as to render a meaningful search of the claims impossible. Consequently, the search has been carried out for those parts of the application which do appear to be concise, namely the method of claim 3 (combined with claim 1 or 2) and the method of any of claims 4 to 8 insofar as they refer at least to claim 3.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/12536

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4975209 A	04-12-1990	US 4820307 A	11-04-1989
		US 5221285 A	22-06-1993
		AT 106472 T	15-06-1994
		AU 3845989 A	12-01-1990
		CA 1331826 A	06-09-1994
		CN 1039456 A, B	07-02-1990
		DE 68915640 D	07-07-1994
		DE 68915640 T	09-02-1995
		EP 0354648 A	14-02-1990
		ES 2055058 T	16-08-1994
		JP 7026321 B	22-03-1995
		JP 3503072 T	11-07-1991
		KR 9305933 B	29-06-1993
		MX 168920 B	14-06-1993
		PH 25255 A	27-03-1991
		PT 90877 A, B	29-12-1989
		WO 8912714 A	28-12-1989
		US 4936865 A	26-06-1990
		ZA 8904487 A	28-12-1990
US 5173201 A	22-12-1992	AU 8199791 A	18-02-1992
		CA 2087985 A, C	24-01-1992
		CN 1060125 A, B	08-04-1992
		CZ 284457 B	16-12-1998
		CZ 9300066 A	11-08-1993
		EP 0540557 A	12-05-1993
		HU 63455 A	30-08-1993
		MX 9100324 A	28-02-1992
		NZ 239069 A	27-06-1994
		PL 297655 A	13-07-1992
		SK 2993 A	09-09-1993
		WO 9201773 A	06-02-1992
EP 0523910 A	20-01-1993	CA 2074059 A, C	19-01-1993
		DE 69215285 D	02-01-1997
		DE 69215285 T	10-04-1997
		JP 2865489 B	08-03-1999
		JP 5239071 A	17-09-1993
		KR 239610 B	01-02-2000
US 5235082 A	10-08-1993	US 5269951 A	14-12-1993
		CA 2112874 A	09-07-1994
		DE 69408546 D	26-03-1998
		DE 69408546 T	25-03-1999
		EP 0606159 A	13-07-1994
		ES 2115154 T	16-06-1998
		JP 6298775 A	25-10-1994

